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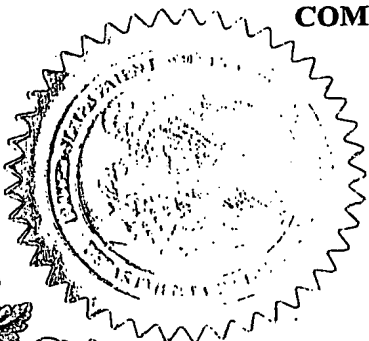
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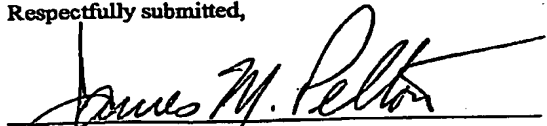
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PROCESS FOR THE PREPARATION OF DEHYDROGENATED HYDROCARBON COMPOUNDS

Background of the Invention

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1) Field of the Invention

This invention relates to the field of hydrocarbon conversion, particularly, the conversion of paraffinic hydrocarbons to olefinic hydrocarbon compounds, and more particularly, the conversion of alkanes and alkylaromatic hydrocarbon compounds to olefins and vinyl aromatic hydrocarbon compounds. In a most preferred aspect, the invention relates to the conversion of lower alkanes, such as, ethane, propane and butanes to olefins, such as, ethylene, propylene and butylenes, and to conversion of lower alkylaromatic hydrocarbon compounds, such as, ethylbenzene, propylbenzene and methylethylbenzene to styrene, cumene and alpha-methyl styrene, respectively.

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15 2) Description of Related Art

It has long been known to dehydrogenate paraffinic hydrocarbon compounds to olefinic hydrocarbon compounds, but the most commercially employed process for producing, for example, ethylene, propylene and butylenes from their corresponding paraffinic hydrocarbon counterparts has been thermal cracking in large, capital and energy intensive facilities. Moreover, the production of vinyl aromatic hydrocarbon compounds by dehydrogenation in fixed bed adiabatic reactors using steam and iron oxide-based catalysts is also well known. However, such processes require an alkylation step to produce the alkylaromatic hydrocarbon compound by alkylating the aromatic hydrocarbon compound with an olefin in the presence of an alkylation catalyst. Such commercially practiced thermal cracking, alkylation and dehydrogenation processes are usually linked by the construction of the alkylation unit closely adjacent to the dehydrogenation unit and, generally, in proximity to a thermal cracker, as a source of olefinic hydrocarbon feedstock.

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More recently, U.S. Patent No. 6,031,143 to Buonomo et al., issued February 29, 2000, describes a process for the production of styrene by feeding an alkylation unit a stream of benzene and a recycled ethylene stream, mixing the outlet stream of the alkylation unit containing ethylbenzene with an ethane containing stream, feeding the mixture to a dehydrogenation unit containing a catalyst capable of contemporaneously dehydrogenating

30

ethane and ethylbenzene, feeding the product leaving the dehydrogenation unit to a separation unit to produce a stream of styrene and an ethylene stream for recycle to the alkylation unit. The dehydrogenation unit is preferably a fluidized bed reactor connected to a fluidized bed regenerator from which the catalyst is cycled between the regenerator and the dehydrogenation unit. In co-pending patent application USSN 10/181106, filed January 24, 2001, by the assignee of this application, there is disclosed an integrated process of preparing styrene using benzene and ethane as raw materials, which process involves feeding ethane and an ethylbenzene containing stream to a dehydrogenation reactor for concurrent dehydrogenation to ethylene and styrene, respectively; separating the dehydrogenation effluent to recover styrene and provide a dilute ethylene stream in ethane, further containing hydrogen; further separating the dilute ethylene stream to recover styrene to high efficiency; feeding the dilute ethylene stream and benzene to an alkylation reactor to obtain ethylbenzene, which is recycled to the dehydrogenation reactor; subjecting the alkylation unit vent stream containing ethane and hydrogen to cryogenic separation, utilizing a turboexpander to recover ethane, which is recycled to the dehydrogenation unit; hydrogen, which is recovered; and energy. While the described processes are effective at integrating the production of styrene and ethylene, which ethylene is recycled for production of ethylbenzene, thus using ethane and benzene as the starting materials for styrene production and effectively de-coupling the production of styrene from the presence or proximity of an light hydrocarbon steam cracker, the dehydrogenation units proposed employ longer residence times and the catalyst is deactivated relatively quickly, subjecting the hydrocarbons present in the reaction zone to the danger of thermal cracking and the formation of excessive amounts of tars and other heavy products. It would therefore be very useful to provide an apparatus and process which minimizes the gas and catalyst residence time in the reaction zone and decreases the formation of tars and heavy products with a resultant increase in conversion and selectivity to desired products.

Brief Summary of the Invention

The above described deficiencies of prior art processes can be overcome by a process for the dehydrogenation of a paraffinic hydrocarbon compound or moiety to produce
5 unsaturated hydrocarbon compounds comprising contacting a gaseous stream containing the paraffinic hydrocarbon compounds at elevated temperature with a dehydrogenation catalyst at short residence times in a short contact time reactor, such as a riser or downer reactor, having a lower end and an upper end to produce a gaseous stream containing unsaturated hydrocarbon compounds. In another aspect of this invention there is described a process for
10 the preparation of vinyl aromatic hydrocarbon compounds in which the process comprises introducing a paraffinic hydrocarbon compound and an alkylaromatic hydrocarbon compound as a gaseous stream into the lower end of a riser reactor and contacting the gaseous stream with a dehydrogenation catalyst comprising gallium, at least one promoter metal and at least one alkali or alkaline earth metal on an alumina support and under process
15 conditions such that a gaseous product stream is produced at the upper end of the riser reactor, the product stream containing a vinyl aromatic compound and an olefinic hydrocarbon compound, and separating the catalyst from the gaseous product stream. In a further aspect of the present invention, the gaseous product stream is separated to remove the olefinic hydrocarbon compound which is sent to an alkylation unit to produce the
20 alkylaromatic compound and the alkenyl aromatic compound from the gaseous product stream is purified to separate the desired product therefrom.

Brief Description of the Drawings

Figure 1 shows a schematic block flow diagram of a preferred aspect of the present
25 invention in which a riser reactor is employed in a single hydrocarbon feed point which may be used for ethane only, ethylbenzene only, or mixed ethane/ethylbenzene feed configuration.

Figure 2 shows a schematic block flow diagram of a preferred aspect of the present invention in which a riser reactor is employed in a multiple feed point and specifically
30 shown is a split ethylbenzene and ethane feed configuration.

Figure 3 shows a schematic block flow diagram of a preferred aspect of the present invention in which a dual riser reactor has both ethane and ethylbenzene feed streams with series catalyst configuration.

Figure 4 shows a schematic block flow diagram of a preferred aspect of the present invention in which a dual riser reactor has a parallel catalyst configuration.

Detailed Description of the Invention

The process of the present invention provides a process for the separate or simultaneous dehydrogenation of a paraffinic hydrocarbon compound, preferably a lower paraffinic hydrocarbon compound, such as for example, an alkane having from 2 to about 4 carbon atoms, and most preferably, ethane, propane and butanes, to the corresponding olefin, namely, ethylene, propylene, and butylenes, respectively, and an alkylaromatic hydrocarbon compound, preferably a lower alkylaromatic hydrocarbon compound, such as for example, ethylbenzene, propylbenzene and methyl ethylbenzene, to the corresponding alkenyl aromatic hydrocarbon compound, namely, styrene, cumene or alpha-methyl styrene, in the presence of a solid, particulate gallium-based dehydrogenation catalyst by introducing the paraffinic hydrocarbon compound and alkylaromatic hydrocarbon compound into the lower end of a riser reactor at dehydrogenation temperature and after a short residence time recovering a gaseous product stream containing unsaturated hydrocarbon compounds. Preferably, the process is useful to prepare styrene and ethylene from ethylbenzene and ethane, respectively. Likewise, cumene and propylene can be prepared from propylbenzene and propane, respectively.

The process of this invention is carried out in a riser reactor. Riser reactors are known and commonly employed in conversion of certain petroleum fractions into gasoline in fluidized bed catalytic cracking (FCC) processes. In an FCC process, a solid particulate catalyst, usually an acidic clay, silica-alumina or synthetic or natural zeolite type of catalyst, is introduced with a carrier fluid to the lower end of a long, cylindrical or tubular reaction vessel together with a petroleum fraction at elevated temperature and moderate pressure. The cracking process occurs in the petroleum as the liquid petroleum is vaporized by the hot catalyst and both rise in the reactor cylinder. At the top of the riser reactor, the catalyst and hydrocarbon product are separated and the gasoline product stream exits via a vent pipe for separation and further processing into gasoline and heating oil fractions. The catalyst settles

in an annular space between the outside wall of the riser tube and an inner wall of the reactor housing through which a stripper gas contacts the catalyst, at a rate which does not prevent settling of the catalyst, and strips off additional petroleum product from the catalyst surface. The catalyst is then sent to a regenerator/reactivator in which the catalyst is

5 contacted with a regeneration fluid, usually an oxygen-containing gas, and, optionally, a fuel source such as a fuel gas like methane, hydrogen or natural gas, for combustion of any remaining hydrocarbons, heavy residuals or tars, and the regenerated catalyst is sent back to the lower end of the riser reactor to contact additional petroleum for cracking.

In a similar manner in the present invention, the alkylaromatic hydrocarbon

10 compound and/or the paraffinic hydrocarbon compound are introduced to the lower end of a riser reactor and contacted by the hot fresh or regenerated catalyst which is pneumatically moved by a carrier gas. As the hydrocarbon compound(s) rise in the cylindrical reactor with the catalyst, the dehydrogenation reaction takes place and at the top or upper end of the riser, the vinyl aromatic hydrocarbon compound and/or lower olefin is separated from the catalyst.

15 The separation is conveniently accomplished by means of a centrifugal impingement separator, such as a cyclone separator, but the separation can be done by any conventional means for solid-gas separations, including filtration and liquid suspension. The riser reactor can be constructed from conventional materials used in FCC or petrochemical processing and is conveniently a steel vessel using an alloy sufficient for containing the hydrocarbon

20 materials of the reaction, considering the temperature, pressure and flow rates employed and may be refractory lined. The dimensions of the riser reactor are dependent on the process design of a processing facility, including the proposed capacity or throughput, gas hourly space velocity (GHSV), temperature, pressure, catalyst efficiency and unit ratios of feed converted to products at a desired selectivity.

25 The catalyst which can be conveniently employed in the present process is a solid particulate catalyst which is capable of fluidization and, preferably, a catalyst which exhibits Geldart A properties, as known in the industry. Particularly preferred is a gallium based catalyst, such as described in EP-A2-0,905,112; EP-B1-0,637,578; US 5,430,211; and US 6,031,143. As described in these references, the dehydrogenation reaction is carried out

30 in gaseous phase operating in a fixed bed or fluidized bed catalytic reactor, with fluidized bed reactors being preferred for their technological advantages, which are known to those skilled in the field. One preferred catalyst for the dehydrogenation reaction is based on

gallium and platinum supported on alumina in the delta or theta phase, or in a mixture of delta plus theta phases, or theta plus alpha phases, or delta plus theta plus alpha phases, modified with silica, and having a surface area preferably less than about 100 m²/g, as determined by the BET method known to those skilled in the field. More preferably, the catalyst comprises:

- i) from 0.1 to 34 percent, most preferably, from 0.2 to 3.8 percent, by weight of gallium oxide (Ga₂O₃);
- ii) from 1 to 99 parts per million (ppm), most preferably, from 3 to 80 ppm, by weight of platinum;
- 10 iii) from 0.05 to 5 percent, most preferably, from 0.1 to 3 percent, by weight of an alkaline and/or alkaline-earth oxide, for example potassium oxide;
- iv) from 0.08 to 3 percent by weight silica;
- v) the balance to 100 percent being alumina.

15 Another preferred catalyst for the dehydrogenation reaction is based on chromium and comprises:

- i) from 6 to 30 percent, preferably, from 13 to 25 percent, by weight of chromium oxide (Cr₂O₃);
- ii) from 0.1 to 3.5 percent, most preferably, from 0.2 to 2.8 percent, by weight stannous oxide (SnO);
- 20 iii) from 0.4 to 3 percent, most preferably, from 0.5 to 2.5 percent, by weight of an alkaline oxide, for example, potassium oxide;
- iv) from 0.08 to 3 percent by weight silica;
- v) the balance to 100 percent being alumina in the delta or theta phase, or a mixture of delta plus theta phases, or theta plus alpha phases, or delta plus
25 theta plus alpha phases.

The catalysts mentioned hereinabove can be used as such or diluted with an inert material, for example, alpha-alumina, possibly modified with oxides of alkaline metals and/or silica, at a concentration of the inert product of between 0 and 50 percent by weight.

Details on the preparation of the aforementioned catalysts and their more preferred species can be found in EP-A2-0,905,112 and EP-B1-0,637,578. Typically, the process of preparing the aforementioned dehydrogenation catalysts comprises dispersing precursors of the catalytic metals, for example, solutions of soluble salts of the catalytic metals, onto the carrier consisting of alumina or silica. An example of dispersion can comprise impregnation of the carrier with one or more solutions containing the precursors of gallium and platinum, or with one or more solutions of the precursors of chromium and tin, followed by drying and calcination. An alternative method comprises ion adsorption, followed by the separation of the liquid portion of the adsorption solution, drying, and activation of the resultant solid. As another alternative, the carrier can be treated with volatile species of the desired metals. In the case of added alkaline or alkaline earth metals, the addition procedure comprises co-impregnation of the alkaline or alkaline earth metal with the primary catalytic metals (that is, Ga and Pt, or Cr and Sn), or alternatively, addition of the alkali or alkaline earth metal to the carrier prior to dispersion of the primary catalytic metals, and thereafter, possible calcination of the solid.

Other suitable dehydrogenation catalysts, based on iron oxide, are disclosed in Japanese Kokai JP 7-328439 and more preferably disclosed in International Patent Application No. PCT/EP00/09196, filed by Snamprogetti on September 19, 2000, naming Rodolfo Iezzi and Domenico Sanfilippo as inventors. In the description of patent application No. PCT/EP00/09196, the iron oxide catalyst comprises:

- (i) from 1 to 60 percent, preferably from 1 to 20 percent, by weight iron oxide;
- (ii) from 0.1 to 20 percent, preferably from 0.5 to 10 percent, by weight of at least one alkaline or alkaline earth metal oxide, more preferably, potassium oxide;
- (iii) from 0 to 15 percent, preferably, from 0.1 to 7 percent, by weight of at least one rare earth oxide, preferably, selected from the group consisting of cerium oxide, lanthanum oxide, praseodymium oxide, and mixtures thereof;
- (iv) the complement to 100 percent being a carrier consisting of a microspheroidal alumina with a diameter selected from those in delta or theta phase, or in a mixture of theta plus alpha phases, or in a mixture of delta plus theta plus alpha phases, modified preferably with from 0.08 to 5.0 weight percent of silica.

The carrier in the preferred iron oxide catalyst more preferably has an average particle diameter and particle density such that the final product can be classified as Group-A according to Geldart (*Gas Fluidization Technology*, D. Geldart, John Wiley & Sons) and a surface area of less than about 150 m²/g, as measured by the BET method known to those skilled in the art.

The process of preparing the iron oxide catalyst described hereinabove can be generally carried out by means of the following steps: (1) preparation of solutions based on derivatives of the components of the catalyst; (2) dispersion of the solution(s) containing the alkaline or alkaline earth metal oxides and rare earth oxides onto the carrier, for example, by impregnation, ion-exchange, vapor deposition, or surface adsorption; (3) drying of the resulting solids at 100°C to 150°C; (4) optionally, calcination of the dried solids at a temperature less than about 900°C; (5) dispersion of the solution containing the iron precursor and, optionally, additional solution(s) containing precursors of the alkaline or alkaline earth metal oxides and rare earth oxides; (6) drying of the resulting solids at 100°C to 150°C, and (7) calcination of the dried solids at a temperature ranging from 500°C to 900°C. To give a specific example, a microspheroidal pseudoboehmite alumina, to which silica (about 1.2 percent by weight) has been added, may be prepared as a carrier having a particle diameter ranging from 5 to 300 microns, by spray drying a sol of hydrated alumina and Ludox™ brand silica. The sample may be calcined at about 450°C for about 1 hour and then at about 1,190°C for about 4 hours in a stream of dry air. The product obtained, consisting of delta, theta, and alpha transition alumina, has a surface area of about 34 m²/g and a porosity of about 0.22 cc/g. The thusly-prepared microspheroidal alumina may be impregnated, using the "incipient wetness" procedure known to those skilled in the art, with an aqueous solution containing potassium nitrate in deionized water, maintained at a temperature of about 25°C. The impregnated product may be dried at about 80°C and then calcined in a stream of dry air at about 650°C for about 4 hours. The alumina modified with potassium oxide may be impregnated with a second aqueous solution containing ferric nitrate and potassium nitrate, then dried at about 120°C for about 4 hours. The impregnated product may be dried at about 120°C for about 12 hours and finally calcined at about 700°C for about 4 hours to yield the supported iron oxide catalyst. Based on the molarity of the solutions and the amount of solution deposited, the weight composition of the formulate

could be suitably prepared to be about 6.6 percent Fe_2O_3 , about 4percent K_2O and carrier complement to 100 percent.

Another preferred dehydrogenation catalyst consists essentially of a mordenite zeolite, optionally, promoted with a metal selected from gallium, zinc, the platinum group metals, or a combination thereof, as described in US 5,430,211. The mordenite is preferably acid extracted and thereafter impregnated or ion-exchanged with one or more metals selected from gallium, zinc, and the platinum group metals, more preferably, gallium. In this catalyst, the total metal loading typically ranges from 0.1 to 20 weight percent, based on the total weight of the catalyst.

The process of the present invention employs the riser reactor to take advantage of the short residence times provided by such a reactor system. The catalysts described hereinabove as useful in the process of this invention are active catalysts which are capable of completing the reaction in a relatively short reaction time. Consequently, if the catalyst is allowed to remain in contact with the hydrocarbon mixture for a longer period than necessary to complete the dehydrogenation reaction, undesirable byproducts are formed from unreacted starting materials or the products formed are degraded by a continued exposure to the catalyst at process conditions. Thus, it has been unexpectedly been found that the use of a riser reactor to limit exposure of the starting materials to the highly active catalyst species is beneficial to the conversion, selectivity and decrease in the amounts of byproducts formed. Further, use of a riser reactor with relatively short contact or residence time decreases the amount of catalyst required for the process. A lower catalyst inventory provides operating and capital advantages compared with prior art processes. The term short or relatively short residence or contact times, as used in this specification, means a residence time or contact time sufficient to dehydrogenate acceptable amounts of starting materials to products without the formation of significant amounts of byproducts. Preferably, short contact times can range from about 0.5 to about 10 seconds and more preferably from about 1 to about 8 seconds for a molecule of hydrocarbon entering the riser reactor at its lower end until that molecule, whether or not converted to product, exits the riser reactor at its upper end. At such short residence times, the temperature of the reaction mixture, which may be supplied in major part by the hot fresh or regenerated catalyst can range from about 500 to about 800°C. In general, the highest temperature in the riser reactor will be found at the lower end of the cylindrical reactor and, as reaction proceeds and the

catalyst and reaction mixture ascends, the temperature will decrease to the upper end of the riser reactor. The operating pressure of the reaction is relatively low, such as, at or slightly above atmospheric pressure. Preferably, the pressure at which the reaction proceeds can range from about 0 to about 50 psig (0 to 3.45 bar gauge), and preferably from about 0 to about 30 psig (0 to about 2.06 bar gauge). In connection with the above operating conditions, the gas hourly space velocity (GHSV) for the present process has been found to range from about 1,000 to about 150,000 normal cubic meters/hr of hydrocarbon feed per cubic meter of catalyst at bulk density. Conveniently, a catalyst to feed ratio of about 5 to about 100 on a weight to weight basis can be employed in this invention. The catalyst is pneumatically moved through the reaction system by a carrier fluid, which is preferably either an inert diluent fluid or one of the reactants in gaseous form. Examples of inert diluent carrier gases are nitrogen, volatile hydrocarbons which do not interfere with the reaction, steam, carbon dioxide, argon and the like. The paraffinic hydrocarbon compounds useful as reactants in the process of the present invention are also preferred carrier fluids and, most preferred are ethane, propane, and butane. The amount of carrier gas required is only that amount necessary to maintain the catalyst particles in fluidized state and transport the catalyst from the regenerator to the reactor. Preferably, the amount of carrier gas employed can range from about 0 to about 0.2 kg gas/kg catalyst. Injection points for carrier gas, especially reactant feed material carrier gas can be made at multiple points along the fresh or regenerated catalyst transfer line connecting the regenerator with the lower end of the riser reactor. The carrier gas will exit the riser reactor with the product gas or through the vent stream of the regenerator. In the case where the carrier gas is also a reactant, a considerable portion of the carrier gas may be reacted and leave with the product gas stream from the riser reactor.

A preferred aspect of the process of this invention can be illustrated by reference to the various figures of the drawing. As illustrated, without limitation, by Fig. 1 for the preparation of ethane only, a tubular cylindrical riser reactor 10, having a lower end 12 and an upper end 14, is connected at its lower end 12 to a fresh or regenerated catalyst transfer line 16 and at its upper end 14 to a product gas exit line 18. Spent or deactivated catalyst is removed from the product gas at upper end 14 by a separation device (not shown) which can be a conventional solid-gas impingement separator, such as a cyclone separator, and the catalyst is sent via spent catalyst transfer line 20 to regenerator 22 which is a reaction vessel

in which combustion air is blown into the regenerator 22 by means of air line 24.

Supplemental fuel is added via fuel line 62 to provide the heat of reaction and necessary sensible heat, including the heat of vaporization in the case of liquid feed in the riser reactor

10. The combustion products from the oxidation of hydrocarbon on the catalyst are

5 removed from the regenerator 22 by means of vent gas line 28. Prior to being sent for disposal or additional heat recovery, the vent gas may be filtered for removal of catalyst

finer and dust by conventional equipment, which is not shown. As a result of the combustion and hydrocarbon removal, the catalyst is regenerated and heated to a

temperature sufficient to dehydrogenate the hydrocarbon feed materials and is removed

10 from the regenerator 22 by means of regenerated catalyst exit line 30. Fluidization is

maintained by injection of a diluent or carrier gas, for example nitrogen, by means of

nitrogen injection lines 24 and 32, and carrier gas injection lines 34, 36, and 38, so that

catalyst is introduced to the lower end 12 of riser reactor 10 where it contacts ethane which is introduced via hydrocarbon feed line 40.

15 In a similar manner and using propane or butane instead of ethane feed material, the process of this invention would dehydrogenate the feed to propylene or butylenes, respectively.

In operation, the process of this invention, illustrated in the preferred embodiment shown in Fig. 1, proceeds by feeding regenerated catalyst at a temperature of from about 600

20 to about 800°C from the regenerator 22 by means of regenerated catalyst exit line 30 into

fresh or regenerated catalyst transfer line 16 with the catalyst being maintained in a fluid

state of a Geldart A solid particulate material by means of fluidizing inert gas, such as

nitrogen, fed through nitrogen injection lines 24 and 32, and carrier gas, which may be inert

(again, such as nitrogen) or a reactant gas, such as a paraffinic hydrocarbon, such as for

25 example, a lower alkane, preferably ethane, propane, or a butane, via carrier gas injection

lines 34, 36, and 38. This catalyst and carrier gas mixture is introduced to the lower end 12

of riser reactor 10 and contacts a hydrocarbon feed in liquid or gaseous form, preferably the

latter, introduced by means of hydrocarbon feed line 40. The catalyst and hydrocarbon feed,

for example, a lower alkane, such as ethane, propane or a butane, or an alkylaromatic

30 hydrocarbon compound, or a mixture of both lower alkane and an alkylaromatic

hydrocarbon compound, contacts the catalyst and rises in the riser reactor 10 with the

catalyst, feed (which by this time has been transformed into a gas) and the carrier gas. As

the catalyst-feed-carrier gas mixture rises in the reactor, the dehydrogenation reaction occurs and the feed is converted into a lower olefin and/or a vinyl aromatic compound, depending on the feed material. As the reaction mixture, containing gas and catalyst, arrives at the upper end 14 of riser reactor 10, the catalyst and gaseous reaction mixture are separated by a solid-gas separation device, such as an impingement separation device which may preferably be a cyclone gas-solid separator, which is conventional and not shown, but which is well known to those of skill in the art of the FCC industry. The separated product gas is sent to recovery and purification and the catalyst is sent for regeneration and re-heating by means of spent or deactivated catalyst transfer line 20. As the spent or deactivated catalyst is introduced into the regenerator 22, it contacts heated combustion air which is introduced by air line 24 and supplemental fuel introduced by fuel line 62, such that the hydrocarbon materials remaining on the surface of the catalyst are burned off and exit the regenerator via vent gas line 28. The combustion process also serves a second purpose and that is to heat the catalyst so that the catalyst can function as a heat transfer agent or medium in the riser reactor 10. As used in this embodiment, the hydrocarbon feed can be either the lower alkane, the alkylaromatic hydrocarbon compound or a mixture of the two.

As seen in Fig. 2, another preferred embodiment is described which is a variant on the process of the present invention, using the same riser reactor 10 configuration as used in the illustration of the invention in Fig. 1, and in which both the lower alkane, such as ethane, is fed to the riser reactor 10 at or adjacent the lower end 12 by means of ethane feed line 44 and the alkylaromatic hydrocarbon compound, such as ethylbenzene, is fed at a higher point in the riser reactor 10, for example at ethylbenzene feed line 42. Thus, the type of reaction illustrated by the process of Fig. 2 is a split feed riser reactor process which produces styrene and byproducts, such as ethylene which can be returned to an alkylation step to react with additional benzene to produce more ethylbenzene. In such an integrated process, the styrene, for example, is produced from ethane and benzene, whereas conventional processing in a radial adiabatic dehydrogenation reactor requires serially produced ethylene from an ethane thermal or steam cracker, which ethylene in turn is reacted with benzene in an alkylation unit to produce ethylbenzene, which in turn is dehydrogenated to styrene monomer. The present invention employs the lower alkane in the fluidized bed riser reactor dehydrogenation process which produces both lower olefin and vinyl aromatic compounds, the lower olefin is separated and fed to an alkylation unit to

produce the alkylaromatic hydrocarbon compound which is then fed to the dehydrogenation reactor. Thus, instead of producing styrene monomer from ethylene and benzene via dehydrogenation of ethylbenzene, the starting materials are ethane and benzene and a light hydrocarbon steam cracker is not required.

5 In another preferred, but non-limiting embodiment of the present invention, the process of this invention is illustrated in Fig. 3. In this embodiment, a dual riser reactor configuration is illustrated in which the riser reactors 10 and 48 are connected in series. As shown in Fig. 3, riser reactor 10 has lower end 12 and upper end 14. Connected to lower end 12 is fresh or regenerated catalyst line 16 and the catalyst is maintained in fluidized state by injection of carrier gas via lines 34 and 36. Hydrocarbon feed material, such as
10 ethane, is introduced to the lower end 12 of riser reactor 10 by means of hydrocarbon feed line 40. At this stage of the process, the configuration is much like that of Fig. 1; however, the product gas from riser reactor 10 in Fig. 3 is fed to a separation and recovery section (not shown) by means of product gas exit line 18 from which a side product gas line 46 leads to
15 an alkylaromatic hydrocarbon compound feed line, such as ethylbenzene feed line 42. Alternatively, both side product gas line 46, which carries primarily the lower olefin produced in riser reactor 10 in addition to byproducts and carrier gas, can be fed separately into a second riser reactor, such as at 48, having a lower end 50 and an upper end 52. Also entering the lower end 50 of second riser reactor 48 is a partially deactivated catalyst line 54
20 which leads from the upper end 14 of riser reactor 10 to the lower end 50 of second riser reactor 48. Carrier gas line 38 can be used to introduce fluidizing carrier gas into partially deactivated catalyst line 54 at one or multiple points along partially deactivated catalyst line 54. As the ethylene and ethylbenzene rise in second riser reactor 48 with the catalyst and carrier gas, the catalyst is at a lower temperature than when initially introduced to the lower
25 end 12 of riser reactor 10. The relatively lower temperature than in riser reactor 10 permits satisfactory reaction rates for the alkylaromatic hydrocarbon compound and prevents over reaction to undesired byproducts, thus decreasing the yield, conversion and selectivity of the dehydrogenation reaction. The upper end 52 of second riser reactor 48 is connected to second product gas exit line 56 and can lead the vinyl aromatic hydrocarbon compound,
30 such as crude styrene monomer contained in the product gases, into the product gas separation and recovery section, which is conventional and not further described or identified herein. Prior to exit from second riser reactor 48, the reaction mixture must be

separated from the deactivated catalyst and this is done in a solid-gas separation device, such as a cyclone separator, not shown. The separated and deactivated catalyst is fed back to the regenerator 22 by means of spent or deactivated catalyst transfer line 20 which in this embodiment leads from the upper end 52 of second riser reactor 48 to the regenerator 22 where the catalyst is regenerated, as previously described. In operation, the process is much like that described in relation to the process illustrated in Figs. 1 and 2, except that the product gas from the upper end 14 of riser reactor 10 is split and a portion is introduced into the lower end 50 of second riser reactor 48. Ethylbenzene is also introduced into the lower end 50 of second riser reactor 48 along with the partially deactivated catalyst via partially deactivated catalyst line 54 and the dehydrogenation of the ethylbenzene proceeds at somewhat milder conditions in second riser reactor 48 than in riser reactor 10. At the upper end 52 of second riser reactor 48, the product gases are separated from the catalyst in a solid gas separator device, such as a cyclone separator (which is conventional and not shown) and the product gases exit via second product gas exit line 56 and the catalyst is sent back to regenerator 22 for regeneration and reheating via spent or deactivated catalyst transfer line 20.

In a still further preferred embodiment of this invention shown in Fig. 4, the reactor/regenerator configuration is similar to that of Fig. 3, except that the second riser reactor 48 has its own catalyst feed and removal transfer lines, namely second fresh or regenerated catalyst transfer line 58 and second spent or deactivated catalyst transfer line 60 which feed active catalyst to second riser reactor 48 and remove catalyst from it and send the deactivated or spent catalyst back to regenerator 22. In operation and as shown in Fig. 4, the catalyst from regenerator 22 is led by regenerated catalyst exit line 30 to either riser reactor 10 or second riser reactor 48 via fresh or regenerated catalyst transfer line 16 or second fresh or regenerated catalyst transfer line 58, respectively. The feed to riser reactor 10 is ethane via hydrocarbon feed line 40 and to second riser reactor 48 is ethylbenzene via ethylbenzene feed line 42. On contact with the catalyst in the riser reactors, the ethane and ethylbenzene are converted into ethylene and styrene monomer, respectively, and the crude gaseous products are separated from the catalyst in gas-solid separators, such as cyclone separators (not shown) and sent to product gas separation and recovery operations (not shown) to produce ethylene for recycle to make additional ethylbenzene and styrene monomer, respectively, in the configuration of Fig. 4. In a similar manner and using

propane or butane instead of ethane feed, the process of this invention would dehydrogenate the feed to propylene or butylenes, respectively; or using isopropyl benzene or methyl ethyl benzene as feed material, the process of this invention would dehydrogenate the feed to cumene or alpha-methyl styrene, respectively.

- 5 Additional configurations of the riser reactor(s) and regenerator can be envisioned by one skilled in the industry which are within the scope and spirit of this invention. The present invention is desired to be limited only by the lawful scope of the appended claims.

WHAT IS CLAIMED IS:

1. A process for the dehydrogenation of a paraffinic hydrocarbon compound or moiety to produce unsaturated hydrocarbons comprising contacting a gaseous stream containing said paraffinic hydrocarbon compounds at elevated temperature with a dehydrogenation catalyst in a short contact time reactor having a lower end and an upper end at short contact times to produce a gaseous stream containing unsaturated hydrocarbon compounds.
2. The process of Claim 1 wherein said paraffinic hydrocarbon compound is an alkane having from 2 to about 4 carbon atoms.
3. The process of Claim 1 wherein said dehydrogenation catalyst is a gallium containing dehydrogenation catalyst.
4. The process of Claim 3 wherein said dehydrogenation catalyst contains a metal promoter selected from manganese and platinum.
5. The process of Claim 3 wherein said dehydrogenation catalyst contains an alkali or alkaline earth metal.
6. The process of Claim 5 wherein said alkali or alkaline earth metal is selected from the group consisting of sodium, lithium, potassium, rubidium, magnesium, calcium, strontium, and barium.
7. The process of Claim 3 wherein said dehydrogenation catalyst is carried by an alumina or alumina silica support.
8. The process of Claim 2 wherein said alkane is selected from the group consisting of ethane, propane, isopropane, butane, isobutene and mixtures thereof.
9. The process of Claim 1 wherein said contacting occurs in a riser reactor.
10. The process of Claim 1 wherein said contacting occurs in a downer reactor.
11. The process of Claim 1 wherein said contacting is carried out at elevated temperature.
12. The process of Claim 11 wherein said temperature is less than about 800°C and more than about 500°C.
13. The process of Claim 11 wherein said temperature is less than about 750°C and more than about 600°C.

14. The process of Claim 1 wherein said contacting is carried out at elevated temperature for a period of from about 0.5 to about 10 seconds.

15. The process of Claim 14 wherein said contacting is carried out from about 1 to about 8 seconds.

5 16. The process of Claim 1 wherein said contacting is carried out at a gas hourly space velocity of from about 1,000 to about 150,000 normal cubic meters/hr of hydrocarbon feed per cubic meter of catalyst at bulk density.

10 17. The process of Claim 1 wherein after said contacting the gaseous stream containing unsaturated hydrocarbon compounds is separated from the catalyst and the gaseous unsaturated hydrocarbon compound is sent for product purification and recovery.

18. The process of Claim 17 wherein said catalyst after separation from the gaseous stream containing unsaturated hydrocarbons is sent for regeneration and recycle to the riser reactor.

15 19. The process of Claim 1 wherein an alkyl aromatic compound is introduced with the paraffinic hydrocarbon into the contacting zone of the riser reactor to produce an alkenyl aromatic compound and an olefin.

20 20. The process of Claim 19 wherein said alkyl aromatic compound is selected from the group consisting of ethylbenzene, isopropyl benzene and alpha-methyl ethylbenzene to produce an alkenyl aromatic compound selected from the group consisting of styrene, cumene and alpha-methyl styrene.

21. The process of Claim 19 wherein said alkyl aromatic compound and said paraffinic compound are introduced into said riser reactor at different points.

25 22. The process of Claim 21 wherein said paraffinic compound is selected from ethane, propane, butane, iso-butane, pentane, iso-pentane and mixtures of these compounds.

23. The process of Claim 22 wherein said paraffinic compound is selected from the group consisting of ethane and propane.

24. The process of Claim 22 wherein said paraffinic compound is ethane.

30 25. The process of Claim 22 wherein said paraffinic compound is propane.

26. The process of Claim 22 wherein said paraffinic compound is a mixture of ethane and propane.

27. The process of claim 22 wherein said paraffinic compound is ethane and said ethane is introduced into the riser reactor below the point of introduction of said alkyl aromatic compound.

28. The process of claim 22 wherein said ethane is introduced at the lower end of the riser reactor at a temperature of from about 750°C to about 650°C and said alkyl aromatic compound is introduced into said riser reactor at a point above the introduction point of said ethane at a temperature of from about 700°C to about 600°C.

29. The process of Claim 28 wherein the reactor is at a pressure of from 0 psig to about 30 psig (0 to about 2.07 bar gauge).

30. The process of Claim 28 wherein the gas hourly space velocity ranges from about 1,000 to about 150,000 normal cubic meters/hr of hydrocarbon feed per cubic meter of catalyst at bulk density and the residence time of the alkyl aromatic compound and the paraffinic hydrocarbon compound ranges from about 0.1 to about 10 seconds.

31. The process of Claim 22 wherein the gaseous product stream is separated from the catalyst by a separation means.

32. The process of Claim 31 wherein said separation means is a cyclone separator.

33. The process of Claim 1 wherein said paraffinic hydrocarbon compound is an alkylaromatic compound.

34. The process of Claim 1 wherein said alkylaromatic compound is ethylbenzene.

ABSTRACT OF THE DISCLOSURE

- 5 A process for the dehydrogenation of a paraffinic hydrocarbon compound, such as an alkane or alkylaromatic hydrocarbon compound, and particularly, ethane and/or ethylbenzene, to produce an unsaturated hydrocarbon compound, such as an olefin or vinyl aromatic compound or mixture thereof, and particularly, ethylene and/or styrene monomer, in which a dehydrogenation catalyst contacts the feed material in a riser reactor at dehydrogenation conditions, the product gases are separated from the catalyst and sent to recovery while the catalyst is sent to regeneration.

PROCESS FOR THE PREPARATION OF DEHYDROGENATED HYDROCARBON COMPOUNDS
 Joseph E. Pelati, et al.
 Dow Docket 62829
 Sheet 1 of 4

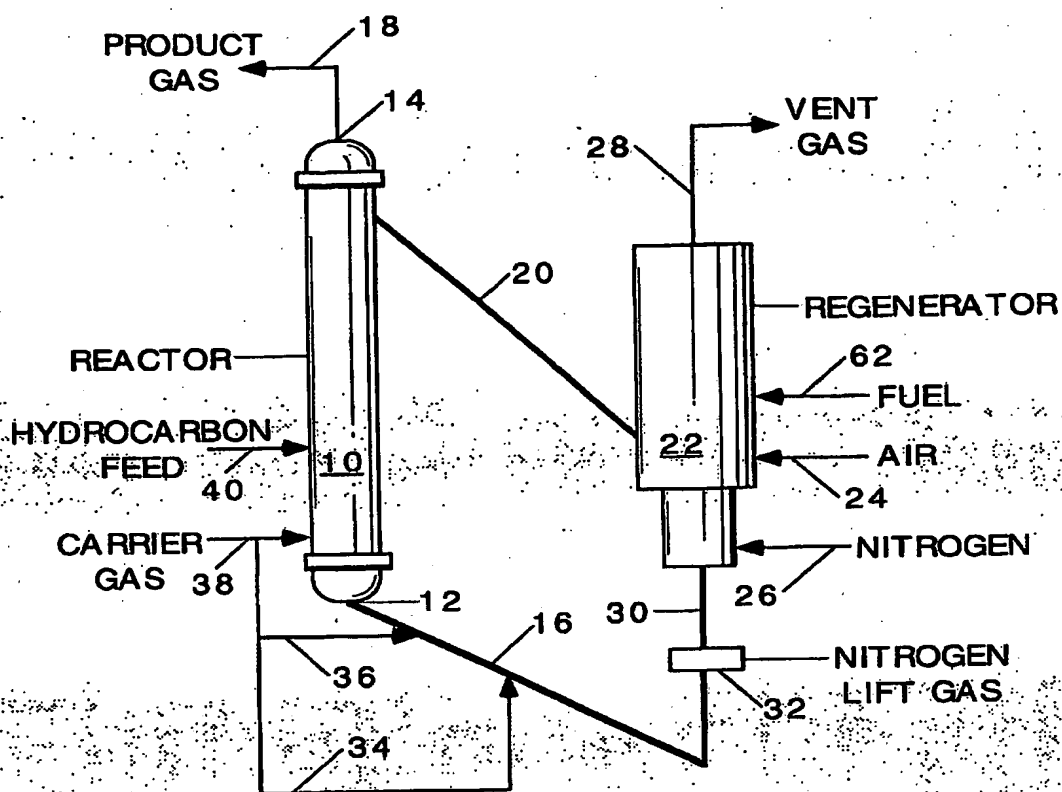


Fig. 1

PROCESS FOR THE PREPARATION OF DEHYDROGENATED HYDROCARBON COMPOUNDS

Joseph E. Pelati, et al.

Dow Docket 62829

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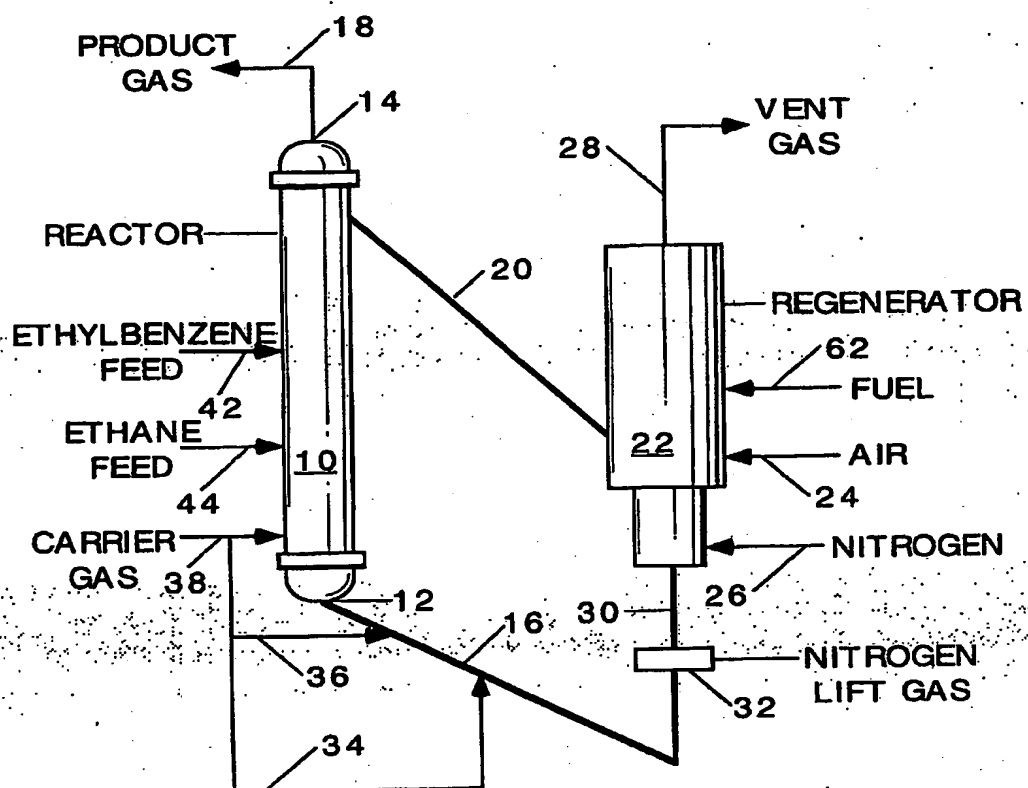


Fig. 2

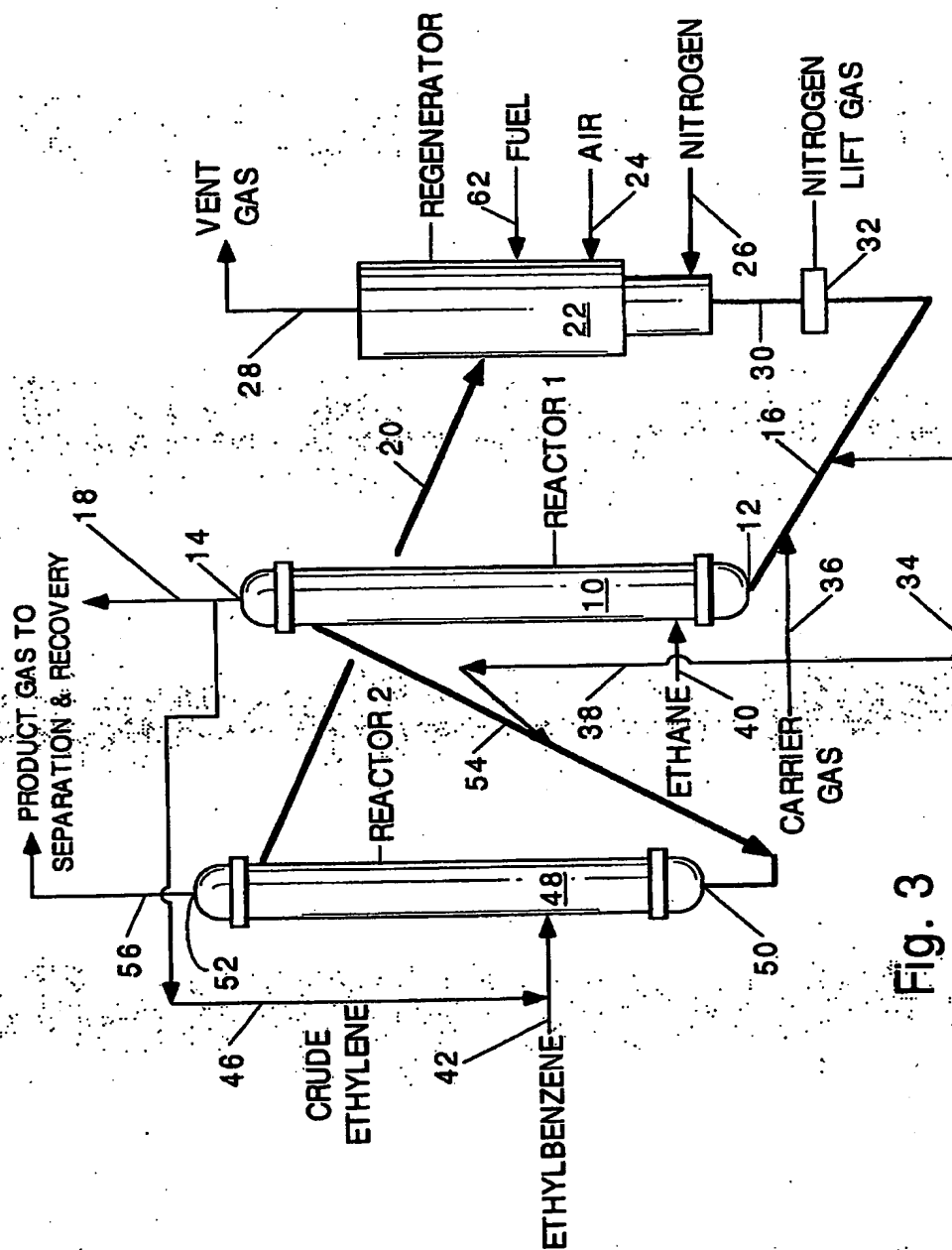


Fig. 3

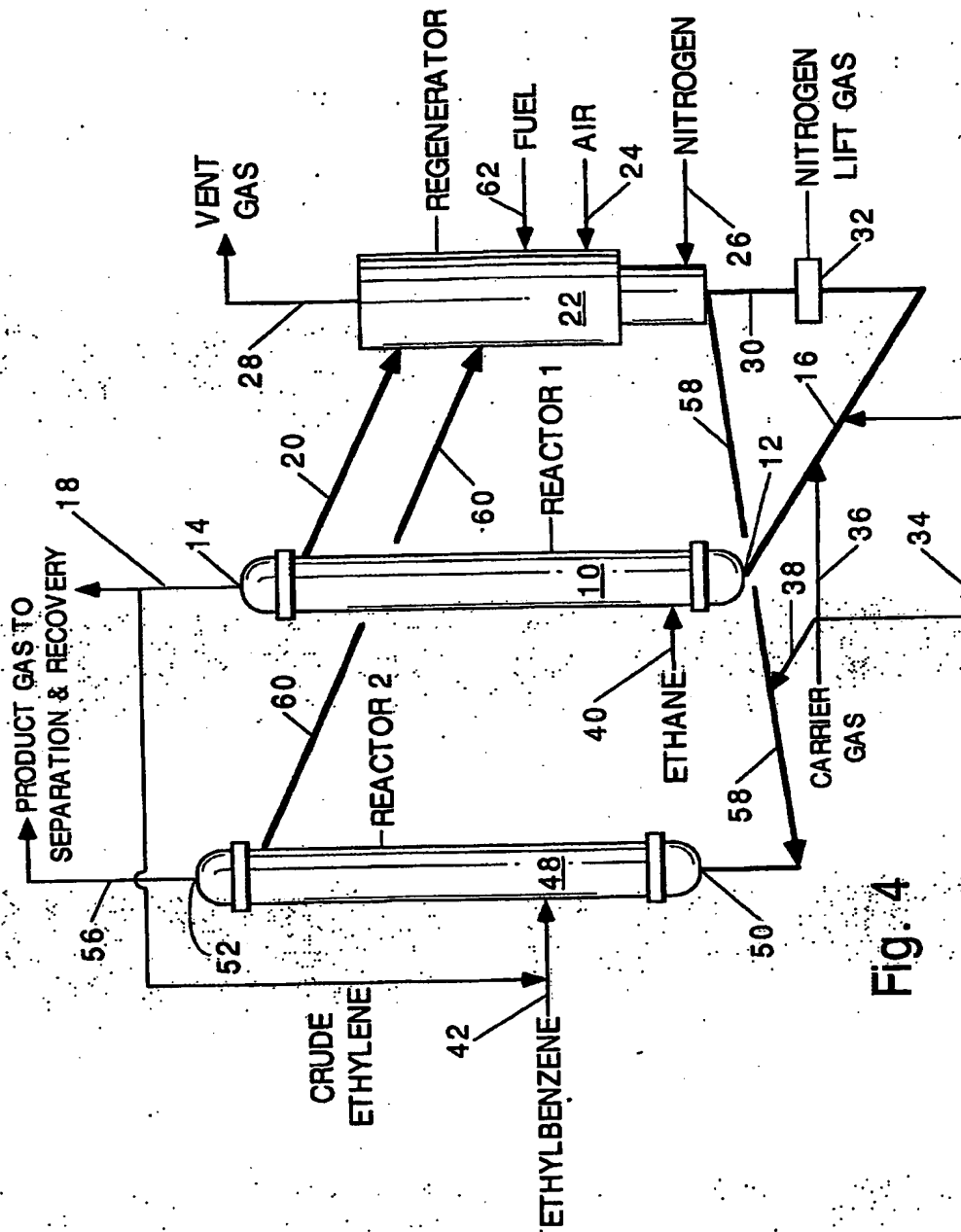


Fig. 4